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QUANTITATIVE MICRO-LUMINESCENCE ANALYSIS
OF LUNAR SURFACE MATERIAL

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The Pennsylvania State University
University Park, Pennsylvania 16802

QUANTITATIVE MICRO-LUMINESCENCE ANALYSIS OF LUNAR SURFACE MATERIALS

by Rustum Roy

Summary Statement

This report summarizes the results of research carried out on lunar samples under this grant. The body of the report consists of papers which resulted from this research, which were presented at the Apollo 12 Lunar Science Conference in January 1971 and have been submitted for publication in the Apollo 12 Lunar Science Conference Proceedings.

The course of the research on the lunar samples was somewhat different from that originally envisioned because of two factors: 1) the lateness in arrival of samples to our laboratory, and 2) the actual nature of the samples. When eventually the samples were obtained, a concentrated effort resulted in the presentation of three papers at the above conference; which have been submitted in the form of four manuscripts for publication. The titles of these papers are listed on page 2. Copies are appended of papers 1, 3 and 4 which were directly supported by the present grant, as well as by funding through an institutional grant NGL-39-009-015 to the Pennsylvania State University, especially Subgrant (34).

Apollo 12 Lunar Science Conference

Rustum Roy + Co-investigators: J. N. Weber, H. K. Henisch, E. W. White
+ Additional investigators: W. B. White, D. M. Roy, B. E. Knox
and G. G. Johnson.

Three papers were presented at the Apollo 12 Conference at Houston, resulting from research sponsored under NASA Grant 39-009-(152), as well as from NGL-39-009-015 (34) grant to the Pennsylvania State University:

- A. R. Roy, D. M. Roy, S. Kurtosy, S. P. Faile and B. E. Knox, "Lunar Glass I: Densification and Relaxation Studies".
- B. H. Görz, E. W. White, G. G. Johnson and R. Roy, "Particle Size and Shape Distribution of Lunar Fines".
- C. W. B. White, E. W. White, H. Görz, H. Henisch, G. Fabel, R. Roy and J. N. Weber, "Lunar Glass II: Structure Analysis by Optical, Raman and X-ray Emission Spectroscopy and Electrical Measurements".

Four papers have been submitted for publication in the Apollo 12 Lunar Science Conference Proceedings, with contents as follows:

- 1. R. Roy, D. M. Roy, S. Kurtosy and S. P. Faile, "Lunar Glass I: Densification and Relaxation Studies".
- *2. B. E. Knox and J. N. Weber, "Glass Formation by Pulsed Laser Interactions with Lunar Surface Materials and Synthetics".
- 3. W. B. White, E. W. White, H. Görz, H. Henisch, G. Fabel, R. Roy and J. N. Weber, "Physical Characterization of Lunar Glasses and Fines". This includes the several sub-papers:
 - a) W. B. White and R. Roy, "Reflectance Spectra of Lunar Fines: Comparison with Synthetic Anorthite Glass".
 - b) E. W. White, W. B. White, H. Görz, R. Roy and J. N. Weber, "Characterization of Lunar Glasses by X-ray Emission and Raman Spectroscopy".
 - c) G. Fabel and H. Henisch, "Evidence of Trapping Levels in Non-Luminescent Lunar Fines".
- 4. H. Görz, E. W. White, G. G. Johnson and R. Roy, "Particle Size and Shape Distribution of Lunar Fines".

*This paper and part of the other work resulted from a related grant to Dr. B. E. Knox.

Lunar Glass I: Densification and Relaxation Studies

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Abstract. In order to provide large quantities of "calibrant" and trial material for several studies, batches of three synthetic compositions simulating lunar glass composition corresponding to typical high titania (A), high iron (B) glasses (Science, Vol. 167, p. 646, Composition B-14 and C-9) and anorthite have been prepared and melted to glasses under varying pO_2 ($10^{-12.5}$ and $10^{-11.2}$).

Following Roy and Cohen's (1961) suggestion, these glasses have been used to give us a model system for determining the magnitude of a pressure event by studying frozen-in density and refractive index changes. The pressure-temperature metastable equilibrium-refractive index dependence of these glasses has been determined in the range from 0 - 65 kb and 50 - 525°C. They show that the changes which are caused are very substantial. For example, Glass A goes from a normal R.I. Value of 1.693 to 1.762 at 45 kb at 400°C and anorthite glass from $n = 1.578$ to $n = 1.668$ at 60 kb, 400°C. The time-temperature conditions needed to relax out these index changes have been determined, and most can be returned to their original value between 500 - 600°C in approximately 1 - 2 hours.

Seven sets of lunar glasses have been relaxed out by temperature annealing, and measurable changes observed. The R.I. is found to increase in some cases (Apollo 11, 10085.49) from 1.662 to 1.675, in others it stayed almost constant, while in other fragments, in the same sample it decreased from 1.673 to 1.660. One lunar glass (10084.110) densified and subsequently relaxed, having an almost identical behavior in both processes to its simulated composition, glass (A). In spite of the use of sealed Pt tubes, it is difficult to avoid changes in valence state. However, the calibrant synthetic glass A does not show any R.I. change in air. In general, it is obvious that the magnitude of the refractive index changes in the lunar samples are very small (and also complicated by compositional and local variations) compared to the major effects obtained at quite low static pressures.

These results are analogous to those obtained of feldspathic glasses by Bell and Chao (1969,1970), von Engelhardt, et al., (1970a) and Chao et al. (1970a). It is clear that the structure and hence, density and refractive index, of non-crystalline solids produced by shock events is not useful as a guide to the actual pressures reached.

INTRODUCTION

Roy and Cohen (1961) first suggested that the densification of glasses could be used as a possible piezometer, for the measurement and recording of pressures in the hundred kilobar region. It is obvious that such measurements and indications of pressure effects can be applied both to laboratory as well as to geologically provided samples. As the literature on shock metamorphism has grown over the last decade we had expected to find evidence that the production of noncrystalline solids at high pressures gave rise to NCS-phases with refractive indices very substantially greater than those of the glasses of the same composition made at atmospheric pressure. However, neither the natural nor laboratory-produced shock metamorphism samples have resulted in very large increases. From the earlier reports of De Carli and Jamieson (1959) to the more recent of Ahrens and Rosenberg (1968) the NCS-phases resulting from laboratory-induced shock metamorphism were not substantially more dense than normally melted glasses. With the discovery that the Apollo 11 samples from the moon contained a large fraction of noncrystalline material, it was hoped that one would be able to possibly determine something of the pressure history of these materials if any refractive index changes could be observed and studied. Further, the magnitude and the kinetics of any relaxation effects in the refractive index values of such glasses could provide interesting clues to the structure of such glasses. The present preliminary report gives data on our research on both these aspects.

PREPARATION OF SIMULATED LUNAR GLASSES

Prior to receipt of the Apollo 12 specimens, and in order to be able to have larger volumes of samples on which to base preliminary experiments, we have prepared a series of synthetic, typical glasses corresponding to pure anorthite, a moderate range ($\text{FeO}+\text{TiO}_2$) content glass, and a high ($\text{FeO}+\text{TiO}_2$) glass.

Glasses were prepared from the compositions shown in Table I by conventional mixing of oxides and carbonates, melting in platinum crucibles, re-grinding and rehomogenization. Glasses A and B were finally equilibrated at a low pO_2 by melting in molybdenum in a partial oxygen pressure corresponding to $10^{-12.5}$ at 1200°C . and $10^{-11.2}$ at 1300°C . respectively. Figure 1 shows these compositions on a summary plot of refractive index vs. composition for a large number of Apollo 11 and 12 glasses studied by Chao et al. (1970b). The glasses A and B were quite homogeneous in refractive index and were both dark brown in color.

Table I

Chemical Composition (in wt%) of Simulated Lunar Glasses

Oxide	(A)	(B)	(C)
SiO_2	43	41	43.19
TiO_2	10	5	
Al_2O_3	10	17	36.65
FeO	19	12	
MnO	0.4	0.2	
MgO	6.5	9	
CaO	9.7	13.3	20.16
Na_2O	0.5	0.1	
K_2O	0.16	0.1	
N_D	1.699	1.648	1.580

Table II

Comparison of Densification Data for Apollo 11
and Simulated High Titania Lunar Glass (A)

Glass Type	Atm	45 kb	65 kb	Relaxed 600°C 1 hr.
Apollo 11 (10085.49)	1.703	1.748	1.762	1.705
Simulated High-Titania (A)	1.699	1.750	1.766	1.705

PRESSURE-TEMPERATURE EFFECTS ON SYNTHETIC GLASSES

The experimental techniques used for these studies have been reported in a series of papers by Cohen and Roy (1962), Dacheville and Roy (1962), and Myers et al. (1963), and will not be repeated here. All high pressure runs are made on prepelleted samples with an aspect ratio of roughly 10:1, surrounded by platinum disks. The temperatures reported are accurate to $\pm 5^\circ$ and the pressure in the opposed anvil system is generally accurate to $\pm 5\%$ of the value in this pressure range. However, in some of the runs made on the actual lunar samples, the volume of the sample was so small that the actual pressure variation is likely to be larger than this. Sample preparation of the lunar glasses for the pressure apparatus was varied slightly from the usual technique because of the necessity of using small sized glass chips, to insure homogeneity. The glass chips studied were placed within a measured amount of SiO_2 powder which would give the desired pellet thickness at the pressures used to prepare the samples for the pressure runs. This method proved quite successful when tested on simulated lunar glass, giving the refractive index of 1.773 for a simulated glass chip of the same size as the lunar fragment compared to a previous index of 1.775 for the normally prepared sample. The change of refractive index, as measured by the Becké line method for Na_2O , with pressure for the three main simulated lunar glasses is summarized in Fig. 2. It should be noted that these are the refractive indices of the glasses after quenching from the stated p-t conditions. These values should represent the "equilibrium" value of the structural state of the particular glass at a given temperature and pressure after release of elastic strain.

The meaning of such curves has been explained in the paper by Cohen and Roy (1961) in their Fig. 4. Several interesting points may be noted in the data shown in Fig. 2. First it is remarkable that the relative change in the index of the three glasses is roughly the same. Second the magnitude of the change is surprisingly high in light of the very moderate pressures involved. Indeed, although we originally planned to carry the work to 200 kilobars, this appeared quite pointless in the light of the actually observed changes in index. Thirdly, the data indicate ^{that} the kinetics of the densification process are a good indicator of the nature of the structural change taking place. In the densification of silica SiO_2 glass, we have previously shown that this process is complete at temperatures in the vicinity of 500°C in a few

milliseconds. However, in certain other glasses the process takes as long as 20-30 hours to reach an equilibrium value at these temperatures (see Cohen and Roy (1962) on densification of soda-magnesium-silica). It is interesting to note from Fig. 2 that there is a substantial change between the values attained in 1.5 hours and those attained after 20 hours in the simulated lunar glasses. Also the data obtained for composition (A) show that there is also a strong temperature dependence of the "equilibrium" refractive index value attained at any particular pressure. The magnitude and direction of this change is quite similar to that observed for SiO_2 .

The magnitude of index change, ca. 0.08 at 60 kb is also comparable to that reported by Chao and Bell (1969) who showed a refractive index increase of ca. 0.04 for an An 68 glass densified at 29.6 kb. These authors did not, however, report data on other types of glass compositions.

In Fig. 3 we show an analogous plot of refractive index vs pressure of the changes induced in real lunar glass samples. (Apollo 10084.110). Several points emerge. First, that the magnitude and sign of the refractive index changes are very similar to those of simulated lunar glass compositions. Indeed, it is striking how closely the real and the simulated samples follow each other in both absolute magnitude of the refractive index and its dependence on pressure. This comparison is brought out in Fig. 3 and even more sharply in Table II. The above results seem to indicate that lunar glasses if produced by shock metamorphism or other processes behave quite normally with respect to their pressure-temperature history. In other words, they show no evidence whatsoever for remanent changes in refractive index which would be caused by transient or static high pressures in excess of a few kilobars.

ANNEALING STUDIES

Before we proceed to a discussion of the densification results, we will report on the relaxation of refractive index as a function of temperature and time, in the densified simulated lunar compositions as well as of Apollo 11 (10085.99) specimens. Figure 4 shows the rate of change of refractive index of the simulated lunar glasses B and C as a function of time at different temperatures. It will be noted that most of the "excess" refractive index is

annealed out within a period of 1 or 2 hours at temperatures in the vicinity of 500-600°C. However even at temperatures in the order of 160-200°C there appears to be a substantial change in a matter of hours in compositions B and C, although A showed no change at 250°C, suggesting that the temperatures attained in the lunar day may be sufficient to permit relaxation. This is a rather unexpected result and may be one reason why no permanent densification has been found. Another factor to consider is that only a small fraction of the maximum shocked density is apparently retained in naturally^{and} experimentally shocked glasses (Bell and Chao, 1970). Recently they investigated naturally densified glasses from the Ries Crater and synthetically shock-wave produced NCS glasses from labradorite crystals (An₆₇). Their data for the latter glasses show greater densification of the glass obtained at 285 kb than for the glass shocked at 325 kb, indicating the importance of the release adiabat over the peak pressure (French and Short (editors), 1968). Though the higher shock pressure gave a lower final densification, the rate of change of index on annealing after the initial drop is lower even when annealing is carried out at a high temperature. The naturally densified feldspar glasses required even shorter annealing times.

Our data in Fig. 4, glass C, also point to an interesting feature that the rate of change of index on annealing is smaller if the glass has previously been allowed to "equilibrate" at the high pressure for the longer times.

Fig. 5 shows the data on the simulated lunar glass A which again shows a very rapid decrease of refractive index with time and on the same figure we also show the results obtained on various lunar glass samples (10085.49) which are chips from the glass lining of cavities. It will be noted that the behavior is quite different for the lunar glasses in that they show only very small changes in index. Some show instead of the expected decrease of refractive index, a very small increase in refractive index at these temperatures. (bottom of Fig. 5.). In one case a decrease in refractive index was observed when a glass chip (10085.49) went from a value of 1.673 to 1.660 at 580°C for two hours. The data have been obtained principally in sealed platinum systems to avoid changes in oxidation state. The glasses have been compared under various oxidizing conditions in order to estimate or avoid changes in refractive index due to changes in valence states. It appears from the data on simulated glasses that oxidation and reduction play a minor role

in the change of refractive indices; this source of possible complication is however, important in discussing the changes in the real lunar samples since the changes involved are so small. See Fig. 4, sample C.

DISCUSSION OF DATA

Analysis and interpretation of the data are far from complete. However, some of the results already suggest certain conclusions. Von Engelhardt et al. (1970a) have earlier reported the increase on annealing in refractive index of the lunar glasses of compositions close to the plagioclases.* They noted that some of the lunar diaplectic plagioclase glasses (as well as glasses from terrestrial impact craters) actually increased their refractive index upon annealing. Bell and Chao (1970), however, reported a negative index change on annealing for densified glasses from terrestrial impact and experimental shock wave events. The maximum change in index of refraction for one impactite (An_{22}) was 0.0076. Later, Chao et al. (1970a) noted that in an anorthite-like glass from Apollo 11 the refractive index decreased from 1.5688 to 1.5674 upon annealing. This decrease in the refractive index is much less than that of 0.013 observed by us for a single dark brown glass chip from (10085.49) (bottom of Fig. 5). Some of our data in Fig. 5 show that in certain lunar glasses high in iron and titania there is virtually no change in refractive index, or only a minor increase.

No effort will be made to review the very substantial literature on static pressure densification of common silicate and borate glasses which has grown up since 1960. Suffice it to report that there is now general agreement that a non-crystalline phase appears to attain a metastable equilibrium configuration (and hence density and refractive index) which is a continuous

* Two additional papers in the present proceedings also describe increases in density and/or refractive index on annealing lunar glasses: Greene et al. (1971) reported a density increase of ~ 0.02 for two glasses annealed at 630° , and Cooper, et al. (1971) described refractive index increases up to 0.0074 on annealing one set of glasses and a density increase of up to 0.033 on another fragment.

function of temperature and pressure. Reasonable values for these effects in a very wide range of compositions are now available for pressures up to roughly 100 kbars. Likewise kinetic data are available both for the densification and the relaxation processes on many glasses. Extreme care must be exercised in measurement and interpretation of all these data, since we are dealing with delicate balances between competing kinetics of reactions among various metastable states.

It is now abundantly clear that the terrestrial and lunar non-crystalline solids (NCS), generally thought to be the product of shock impacts, do NOT show remanent effects which would place them on the same scale as the static data. Indeed it is generally unwise to attempt to relate changes in solids caused by shock pressures quantitatively to those produced by static pressures (Roy, 1969). Instead one may perhaps attempt to understand qualitatively the structural changes in NCS produced by various means. Thus one of the major puzzles is the frequent observation of lunar NCS increasing their refractive indices very substantially on annealing.

Increases of such magnitude in the refractive index of a normal glass upon annealing are extremely rare. Recently Rindone (1965) reported a similar finding in some high index high-titania glasses. He ascribed such changes to a change in coordination of Ti^{4+} from four to six. Although two of our samples do contain considerable Ti, this obviously cannot be the correct explanation since the near plagioclase-compositions reported on by von Engelhardt (1970a) show the same phenomenon.

One possibility suggested by our own work by laser-Raman spectroscopy on some of the same lunar samples, is the incipience of crystallization (W.B. White et al. This volume, 1971). Impact glasses are known to contain crystalline inclusions (O'Keefe, 1963) and certainly these lunar NCS show a wide range of not only compositional but structural inhomogeneity. It is conceivable that phase separation and subsequent growth to sub-x-ray-detection size could cause such refractive index changes.

It is quite obvious that lunar glasses contain little record of the pressures reached in various events on the lunar surface as part of their permanent refractive index. Indeed, the puzzle that now confronts the crystal chemist is how the dynamic high pressure gives rise to a non-crystalline

solid - i.e. how shock amorphization works on an atomic scale. One route is by the process of low temperature stepwise reaction of a high pressure phase to the equilibrium phase whereby for example, Dachille, Zeto and Roy (1963) converted stishovite to a NCS by low temperature annealing. The observation of the effect of an increase of refractive index upon annealing would suggest alternatively that the process responsible for the destruction of crystallinity is not the high pressure part of the shock cycle. It is possible to conceive of the destruction of a structure which does not undergo a phase transition, by the rarefaction wave as the lattice is subjected to the high negative pressure expansion of the lattice and propagation of all surface defects and dislocations throughout the crystal. Such disorder cannot subsequently be reversed in the compression part of the cycle - glasses typically do not crystallize under shock pressures. Of course, the destruction of crystallinity may also be ascribed merely to excessive heating in the shock wave. The preliminary laser experiments (Knox and Weber, 1971) suggest that there are threshold energies both for melting and for the development of the globular morphologies observed. In any case it would appear that the thermal or thermal-simulating processes dominate the thermodynamic environment which produced the lunar glasses.

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Rustum Roy and Della M. Roy are also affiliated with the Departments of Geochemistry and Mineralogy and of Materials Science.

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Figure Legends

- Figure 1. Composition and refractive index of lunar glasses of impact origin (after Chao et al., 1970b).
- Figure 2. Pressure densification of simulated lunar glasses.
- Figure 3. Comparing pressure densification of Apollo 11 (10084.110) and simulated lunar glass (A).
- Figure 4. Annealing of simulated lunar samples (B) and (C).
- Figure 5. Annealing of Apollo 11 (10085.49) glass and simulated lunar sample (A).

COMPOSITION AND REFRACTIVE INDEX OF LUNAR GLASSES OF IMPACT ORIGIN

[After Chao et al. (2)]

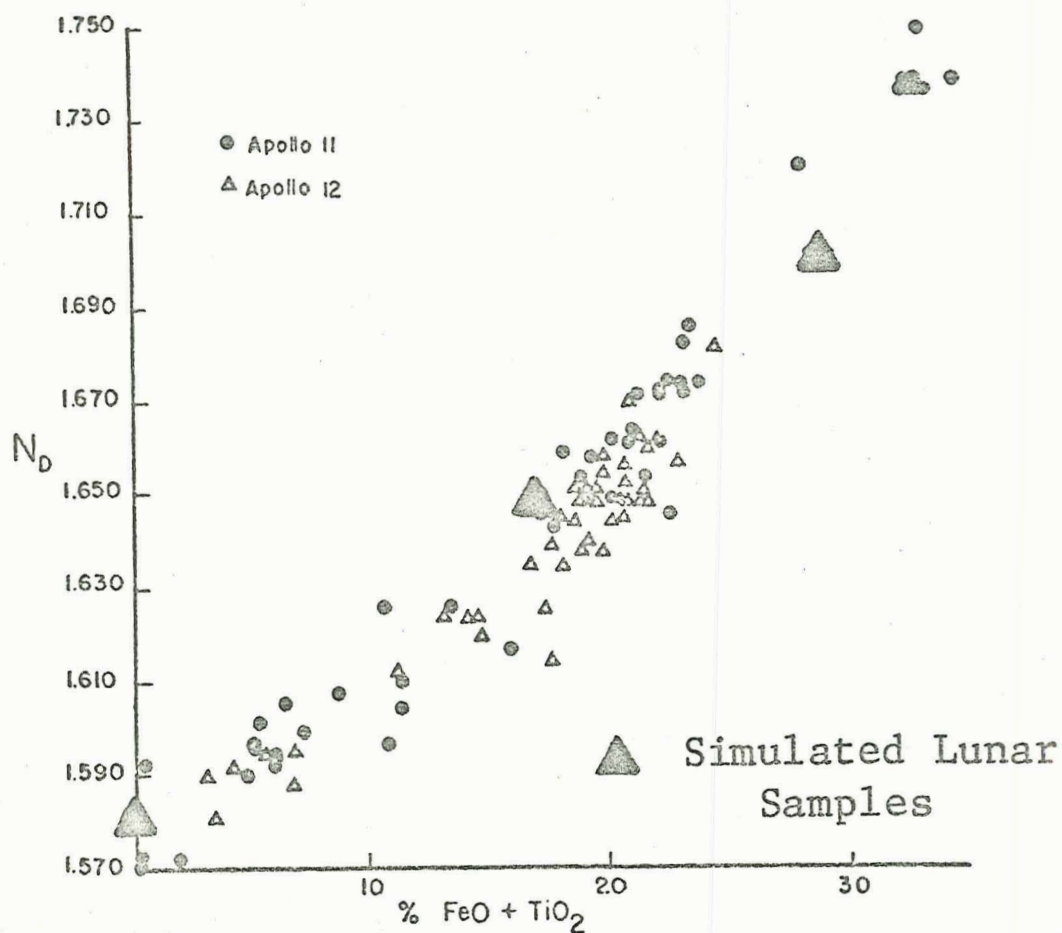


Fig. 2

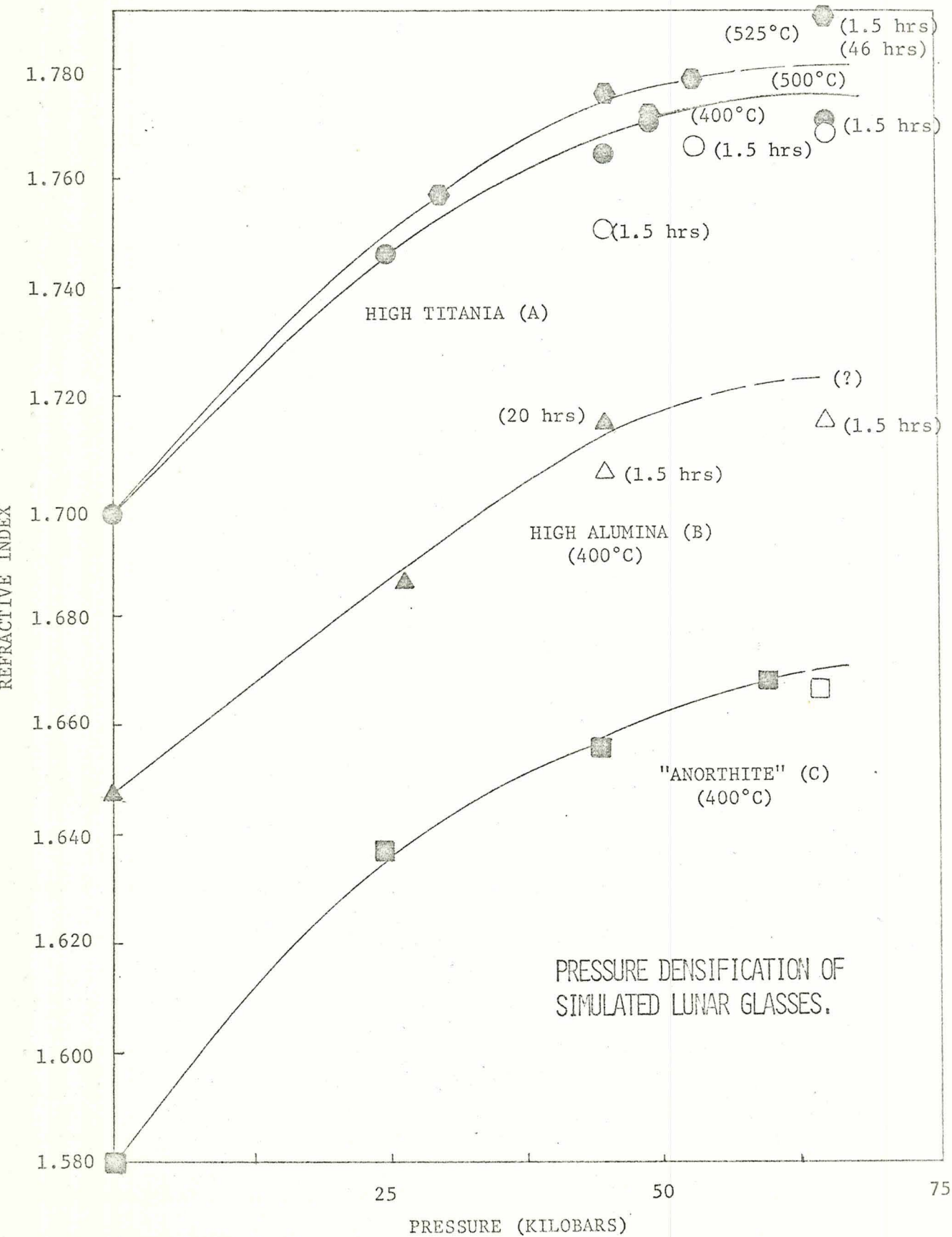


Fig. 3

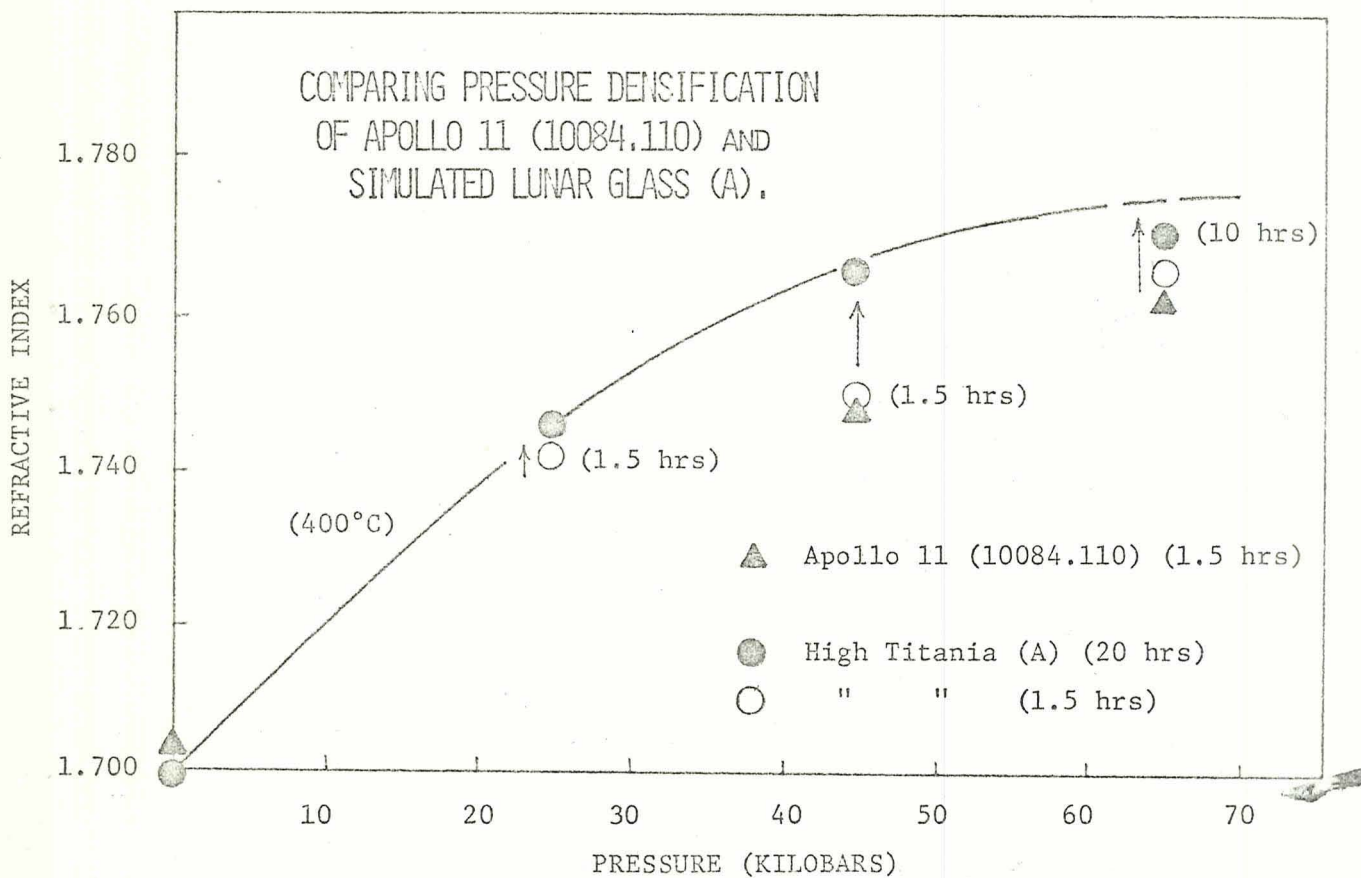


Fig. 4

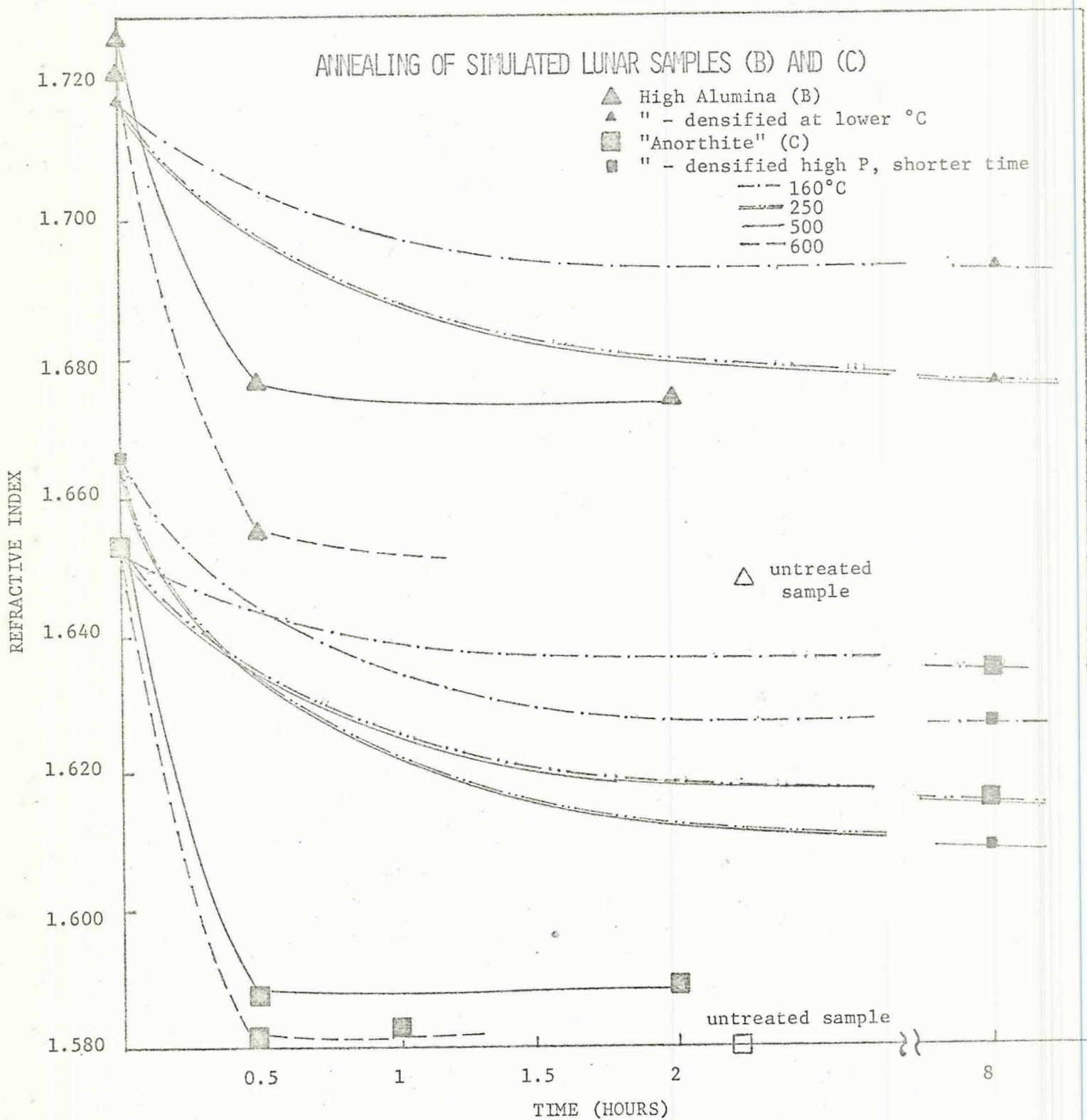
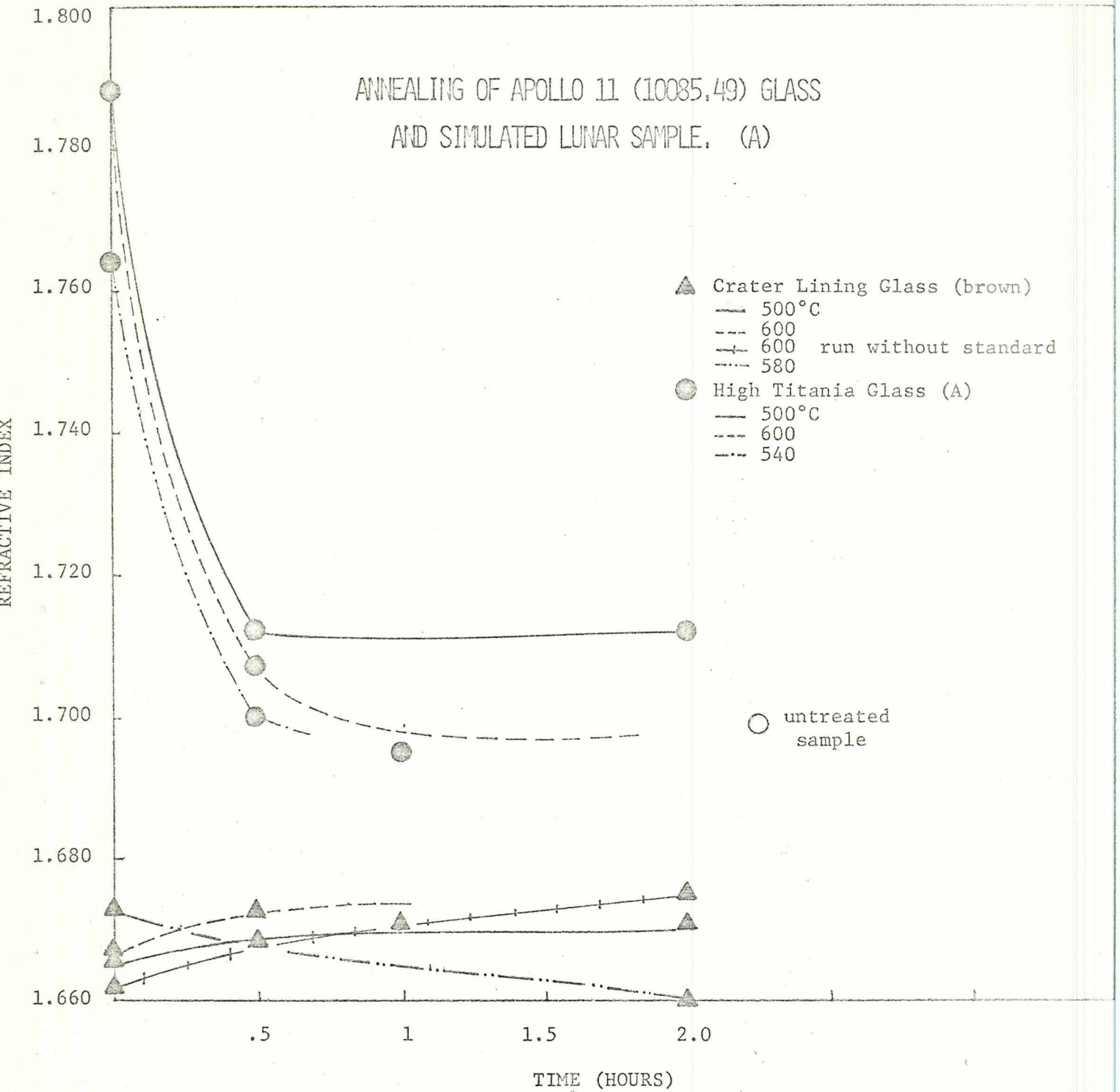


Fig. 5



PHYSICAL CHARACTERIZATION OF
LUNAR GLASSES AND FINES

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ABSTRACT

Lunar fines and glasses from Apollo 11 and Apollo 12 samples have been characterized by diffuse reflectance, Raman spectroscopy, x-ray emission spectroscopy and thermally stimulated currents. Diffuse reflectance, in agreement with other workers, shows Apollo 12 fines to be more reflecting than Apollo 11. Comparison with spectra of synthetic anorthite glass shows that the glassy component of the fines may well contribute to the dark background absorption but does not superimpose absorption bands. Thermally stimulated current and thermally stimulated depolarization measurements show the existence of low temperature traps in the lunar fines and offers an alternative route to trap characterization in non-luminescent specimens. Individual fragments of lunar glass from Apollo 11 and Apollo 12 have been examined by x-ray emission and Raman spectroscopy. The glass fragments are very heterogeneous. Both methods indicate unusual structures in the glass and many of the glass fragments show incipient crystallization as evidenced by sharp bands in the Raman spectrum.

INTRODUCTION

Physical properties of lunar fines and lunar glass from Apollo 11 and Apollo 12 localities have been measured. In the case of the unsorted lunar fines, the object was to obtain information about the electronic behavior of the bulk material and in particular, the contribution of the glass to the optical properties. In the case of the glass, the object was structural characterization, by non-destructive methods. Glass structure is difficult to determine under any circumstances and is doubly so for the lunar glass because of small sample size and heterogeneity.

DIFFUSE REFLECTANCE SPECTRA

Studies of the reflectance spectra of lunar soil from the Apollo 11 material show a rather monotonously increasing absorption from the near infrared through the visible. The smooth curve is broken by two pronounced absorption bands, one at 940 nm, and a weaker one near 1900 nm. (ADAMS and MCCORD, 1970; BIRKEBAK, CREMERS, and DAWSON, 1970). The absorption features were associated with the characteristic spectrum of Fe^{++} in clinopyroxene.

In the present study, we examine the diffuse reflectance spectra of three specimens of lunar soil from Apollo 12 and compare the spectra with one specimen from Apollo 11. In particular, we are concerned with the role of glass in the lunar fines and have therefore also compared the spectra of the lunar materials with spectra of several synthetic glasses containing iron and titanium.

Diffuse reflectance spectra were obtained on a Beckman DK-2A spectrophotometer with an integrating sphere attachment. The sphere was coated with BaSO_4 paint and BaSO_4 was used as a reference. Spectra of the synthetic glasses were obtained on a Cary model 14 spectrophotometer in the trans-

mission mode using polished slabs of glass.

The Lunar Fines

Reflectance spectra obtained from pressed pellets of lunar fines are shown in Figure 1. The absorption spectra from the Apollo 12 site are all remarkably similar. The absorption of the material from the Apollo 11 site is distinctly higher (i.e. the reflectivity is lower) as has also been noticed by other workers concerned with the spectra of the lunar fines (ADAMS, 1971; BIRKEBAK and DAWSON, 1971; GARLICK et al., 1971). There appears a distinct absorption feature at 940 nm which seems to be somewhat more intense in the Apollo 12 material than the equivalent feature in the Apollo 11 material. The expected spectral feature at 1900 nm appears as a broad and rather indistinct shoulder. The small dip that occurs in the spectra at this wavelength is an artifact caused by water absorption in the instrument. No additional features that can be specifically correlated with iron or titanium crystal field or charge transfer absorption can be distinguished.

Synthetic Glasses

Spectra of three synthetic glasses are shown in Figure 2. The base glass had the anorthite composition, $\text{CaAl}_2\text{Si}_2\text{O}_8$. To the base glass was added the specified concentration of FeO and TiO_2 . Glasses were melted in molybdenum crucibles at 1700°C for 30 minutes. Spectra were measured on polished slabs of glass.

The characteristic band of 6-coordinated Fe^{++} occurs at 1080 nm in anorthite glass. A shoulder at 1850 nm does not usually appear in glass spectra

and many indicate Fe^{++} in some other coordination. When titanium is the only transition metal present, a Ti^{+++} band occurs at 430 nm in the visible. When both Fe^{++} and Ti^{+++} are present in the glass, the 1080 band of Fe^{++} still appears, but the titanium band is washed out and only a monotonically rising absorption curve appears in the visible. The long tail of this absorption feature extends into the near infrared with the iron band superimposed on it. This continuous background absorption is due to charge transfer processes between titanium atoms and between iron and titanium.

Origin of Spectra

The reflectance spectra of the lunar fines may well contain a contribution from charge transfer processes between the various valence states of iron and titanium in the lunar glasses. The absorption bands that appear superimposed on the monotonic background appear to be due mainly to Fe^{++} in the distorted M2 site of the pyroxenes. Low-calcium ortho- and clinopyroxene both have characteristic bands near 900 nm, while high-calcium pyroxenes, olivine, and the glass all have the octahedral iron band above 1000 nm (BURNS, 1970; LEWIS and WHITE, in press). The coincidence of the rather broad absorption maxima, however, does not exclude the possibility that some contribution comes from the iron in the glassy phases.

Titanium does not appear to give a distinct band in the bulk spectra of the lunar fines. Such absorption if present is lost in the general charge transfer (or coloration from radiation damage centers) background. Only Ti^{+++} would give a crystal field band. Ti^{4+} does not have an absorption band of its own although it contributes very strongly to the charge transfer

processes. The general increase in reflectance in the Apollo 12 lunar fines correlates rather well with the lower titanium concentrations. Also lower, of course, are all of the hosts that carry the coloring ions -- opaques, pyroxenes, and glasses. The feldspars generally do not accept the coloring ions in solid solution.

THERMALLY STIMULATED CURRENTS AND THERMALLY STIMULATED DEPOLARIZATION

Several workers (DALRYMPLE and DOELL, 1970; HOYT et al., 1970; GEAKE et al., 1970) have demonstrated the presence of trapping levels in Apollo 11 samples by thermoluminescent measurements performed above room temperature. (BLAIR and EDGINGTON, 1970 and BLAIR et al., 1971) found a thermoluminescent glow peak below room temperature (near -135°C) in sorted fractions of Apollo 11 and Apollo 12 fines. They also reported the presence of a water-induced glow peak at -90°C which could be annealed out by heating above 200°C .

In the present investigation on unsorted fines, no thermoluminescence was detected in the temperature range -190°C to 100°C . The study of trapping levels in near-insulating materials of this type is severely limited by a shortage of applicable experimental procedures. One method which has been applied to such solids is the measurement of thermally stimulated currents (TSC). However, the interpretation of these measurements is hindered by a voltage dependent conductivity which arises from contact resistance and space-charge controlled processes in the bulk (HENISCH and FABEL, 1970). Alternative procedures, which are free from some of the difficulties associated with non-ohmic behavior, depend on electret processes (FABEL and HENISCH, 1970). These regard the material as a medium for polarized charge

storage. The amount of charge that can be stored is a measure of the trap density and the temperature at which the overall dipole is discharged is (in the most general terms) a measure of the trap depth. Although a quantitative assessment of trapping levels by either of the above methods is not likely to be straightforward, the methods can be reliably used as sensitive detectors of the presence of trapping levels in near-insulating materials.

Measurements

A powder sample of lunar fines (No. 12057, 63) was pressed into a pellet 1 cm in diameter and 0.2 cm thick. To explore the possibility of trap characterization in this near-insulating specimen, the methods of thermally stimulated currents (TSC) and thermally stimulated depolarization (TSD) were employed. The sample was far from ideal for measurements of this kind, but since the specimen was found to be non-luminescent, a characterization of its trapping levels could be performed only by electrical methods.

The TSC measurements were performed in the usual manner. The pressed sample was cooled to -190°C and irradiated with UV (3650\AA) for a pre-determined time interval. After irradiation, a field of 250 v/cm was applied across the pressed pellet and the current was monitored while the temperature of the specimen was increased at a linear rate ($30^{\circ}\text{C}/\text{min.}$). A current maximum at approximately -5°C was recorded for all UV exposure times tested (Fig. 3a). The magnitude of this peak varied within wide limits for a given irradiation dosage, presumably as a result of changes in the inter-

granular contact conditions. However, the temperature of the peak varied from measurement to measurement by only a few degrees. In some cases an additional peak was recorded near 40°C but this could not be reproduced consistently.

For TSD measurements, the specimen was irradiated with UV at -190°C while in the presence of a large electric field (2500 v/cm). The UV and then the field were removed and the specimen stored for 15 minutes at -190°C before depolarization was measured. The specimen was then connected to the electrometer and the discharge was monitored while the temperature was increased at a uniform rate. The depolarization curve possessed one broad peak at approximately the same temperature and one at 80°C (Fig. 3b). A smaller depolarization was recorded when the electret was formed without UV irradiation, i.e. by application of the field alone.

The peak at -5°C in the TSC glow curve can be explained by carrier release from a single trapping level in the bulk or a closely bunched set of levels. A corresponding maximum in the TSD curve supports this hypothesis. The TSD method generally yields better resolution than TSC (SEMAK et al., 1967). However, because of the nature of the space-charge polarization process, it favors the surface regions (versus bulk), and the broad response in Fig. 3b suggests that these are highly disturbed. Presumably this is due to the bombardment the material had received in the lunar environment.

For a sample of this type, a quantitative analysis of the above results would not be straightforward. The usual problems associated with electrical measurements on near-insulating materials as discussed above apply, of course, in this case. However, the fact that structure of the

kind given in Fig. 3 can be revealed shows that the methods employed are intrinsically capable of useful application.

X-RAY EMISSION WAVELENGTH SHIFTS

Aluminum, silicon and oxygen x-ray emission band spectra were recorded for a series of lunar glasses and a simulated lunar glass in two stages of densification.

The $AlK\beta$ and $SiK\beta$ bands were recorded as reported earlier by (WHITE and GIBBS, 1967, 1969). The oxygen $K\alpha$ emission band shifts were recorded as described in the work by (GIGL et al., 1970) and were measured with respect to an α -quartz standard. All spectra were obtained using an Applied Research Laboratories electron microprobe model EMX operated at 20 KeV and from 0.10 to 0.20 μA specimen current. A large spot diameter ($\sim 100 \mu m$) was used throughout. Specimens were prepared as polished grain mounts using Lakeside 70 cement. Shift (Δ) measurements for $AlK\beta$ and $SiK\beta$ are precise to about ± 5 , whereas the $\Delta OK\alpha$ values are good to about ± 15 .

There are significant shifts in all three emission bands among the lunar glass specimens, but no extensive interpretation can be made at this time for lack of descriptive data on the specimens. Interpretation is further complicated by the inhomogeneous nature of the glasses.

Table 1 summarizes the results from the glasses.

The magnitude of the $AlK\beta$ shift (arbitrarily measured with respect to $\alpha-Al_2O_3$ as used in the (WHITE and GIBBS paper, 1969) is about the same as obtained from the synthetic glasses.

The average $\text{SiK}\beta$ shift (measured with respect to α -quartz) is on the order of 0.0040\AA , corresponding to a mean Si-O tetrahedral bond length of about 1.630\AA . The shift (Δ) of 65 for the glass from 10085.49 is the highest we have found for any silicate material. Most noteworthy of the $\text{SiK}\beta$ shift data is the large change with densification of the synthetic glass. If one can assume that this is due to changes in the Si-O bond lengths, then this represents a change from a value of about 1.615\AA for the less dense glass to about 1.635\AA for the densified material. If these tentative data are correct, then it means that the Si-O bonds are relatively more affected by changes in glass density than are the Al-O bonds. The large $\Delta\text{SiK}\beta$ and $\Delta\text{OK}\alpha$ values for the 10085.49 glass may possibly indicate an unusually large degree of covalency in the Si-O bonds.

RAMAN SPECTRA

Raman spectra were measured on individual spheres or shards of glass, using a Spex Ramalog double spectrometer with an ionized-argon laser source. The 488 or 514.4 nm lines of the laser can be focused to an area of less than 0.01 mm^2 so that measurements could be made on individual particles. The Raman scattered light was observed at 90° to the incident beam. The glass particles were placed at the focal point supported by a thin cast collodion tube which itself gave no spectrum under measurement conditions.

Glass spectra are extremely weak under all conditions and the dark lunar glasses gave extremely feeble spectra because of poor beam penetration. The Raman spectrum, however, appears to be very sensitive to traces of crystalline phases or to incipient crystallization of the glass. The presence of crystals gives rise to numerous sharp bands superimposed on the

low-frequency scattering curve. Figure 4 shows spectra of two black glassy spheres from sample 10084. One appears to be completely glassy with only faint suggestions of spectral features (solid lines). The other (dashed lines) is partly recrystallized and shows a complex set of sharp bands in the low-frequency region. This variation from one particle to the next was observed in most of the glassy samples. Many particles of "glass" were shown by the Raman spectra to be partly crystalline.

Figure 5 shows some representative spectra of several kinds of lunar glass. Apollo 11 sample 10084 contained tiny irregular fragments of highly vesicular green-black glass. The significant features are the bands near 1200 to 1300 cm^{-1} and the weak broad features at 850 and near 750 cm^{-1} . These represent stretching and bending vibrations respectively of the SiO_4 tetrahedra. Different fragments of the same glass from the same sub-sample gave quite different Raman spectra and one showed some evidence of crystallization. One of these glasses yielded a stretching frequency at 1250 cm^{-1} , while the second fragment exhibited two such bands. The shards of clear green glass, one from 10084 of Apollo 11 and one from Apollo 12 gave rather similar spectra with identical stretching frequencies.

Both stretching frequencies are usually high. Raman data on silicate glasses are extremely sparse, but such data as exist indicate that the highest stretching frequency observed is at 1200 cm^{-1} in fused silica. The addition of alkali to the silica generates a new band at 1100 cm^{-1} and the 1200 cm^{-1} band disappears (HASS, 1970).

These data are preliminary, but indicate (i) that reasonable-quality Raman spectra can be obtained from non-ideal samples such as the specks of lunar glass, (ii) that there is an extreme degree of variability and hetero-

geneity among the particles of lunar glass from the same split of the same sample, and (iii) that true glass is rare: Most specimens, even those that appear microscopically to be glass, show Raman evidence for some crystallinity.

Raman spectra measured on synthetic anorthite, albite, and silica glasses show only broad spectral features. In particular, the aluminum-containing feldspar glasses show very broad smeared-out scattering in the $900 - 1200 \text{ cm}^{-1}$ region, indicating that the stretching motions of SiO_4 and AlO_4 tetrahedra are mixed by the glassy structure. The sharp bands in this spectral region of the lunar glasses become even more puzzling and their final interpretation must await further work.

Acknowledgments

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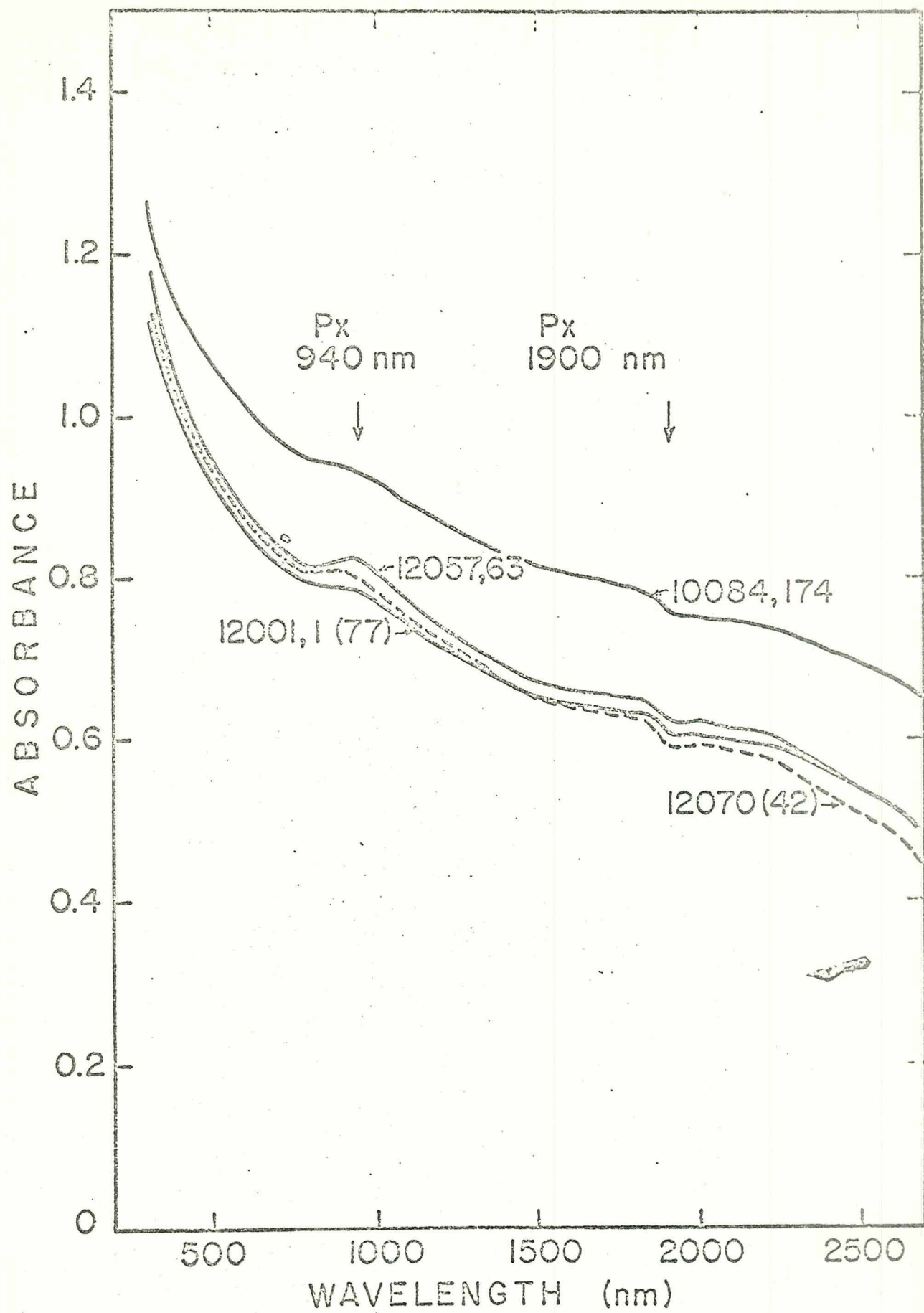
X-RAY EMISSION SHIFT DATA FOR GLASSES

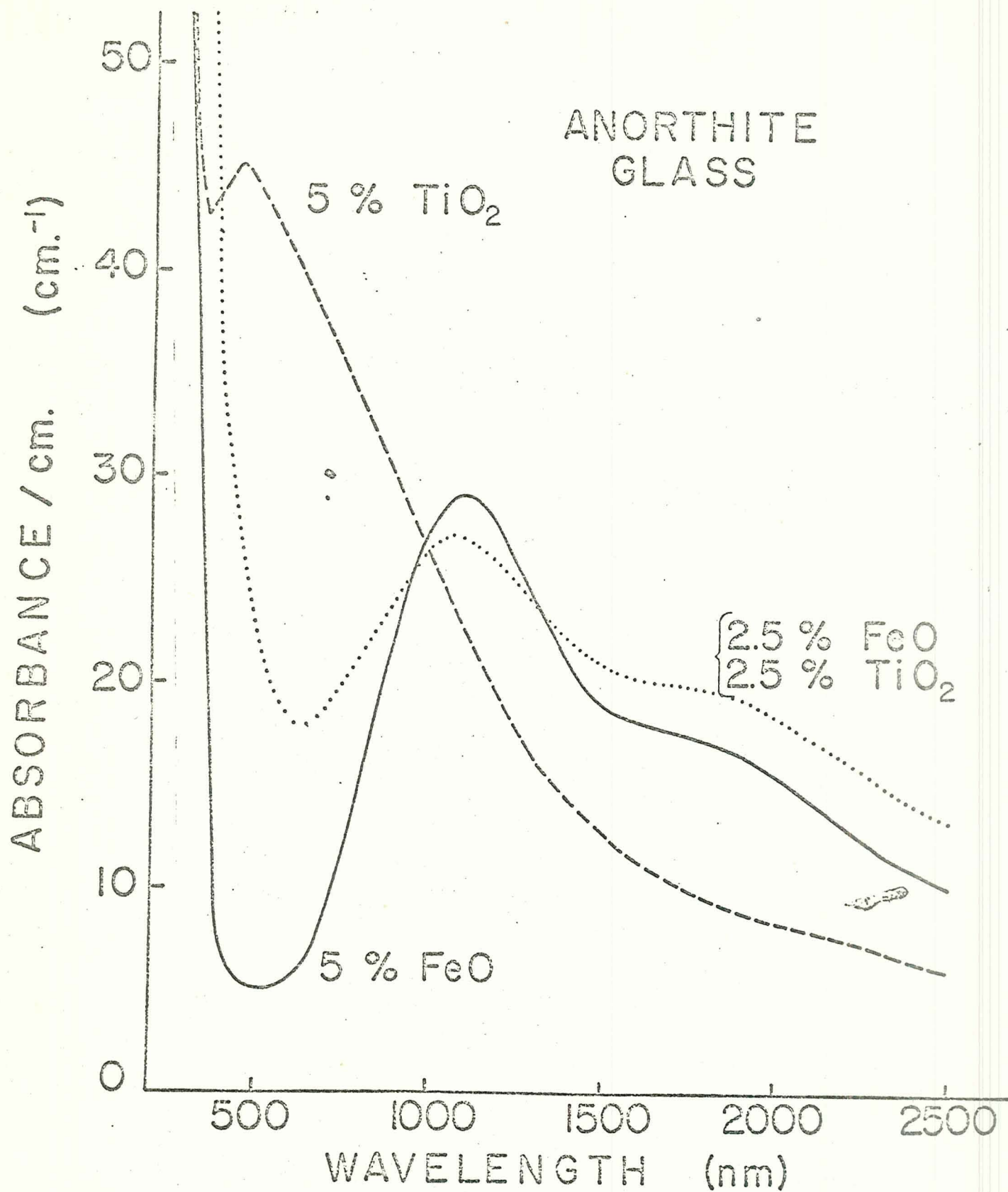
All Shifts (Δ) Recorded as $\text{\AA} \times 10^{-4}$

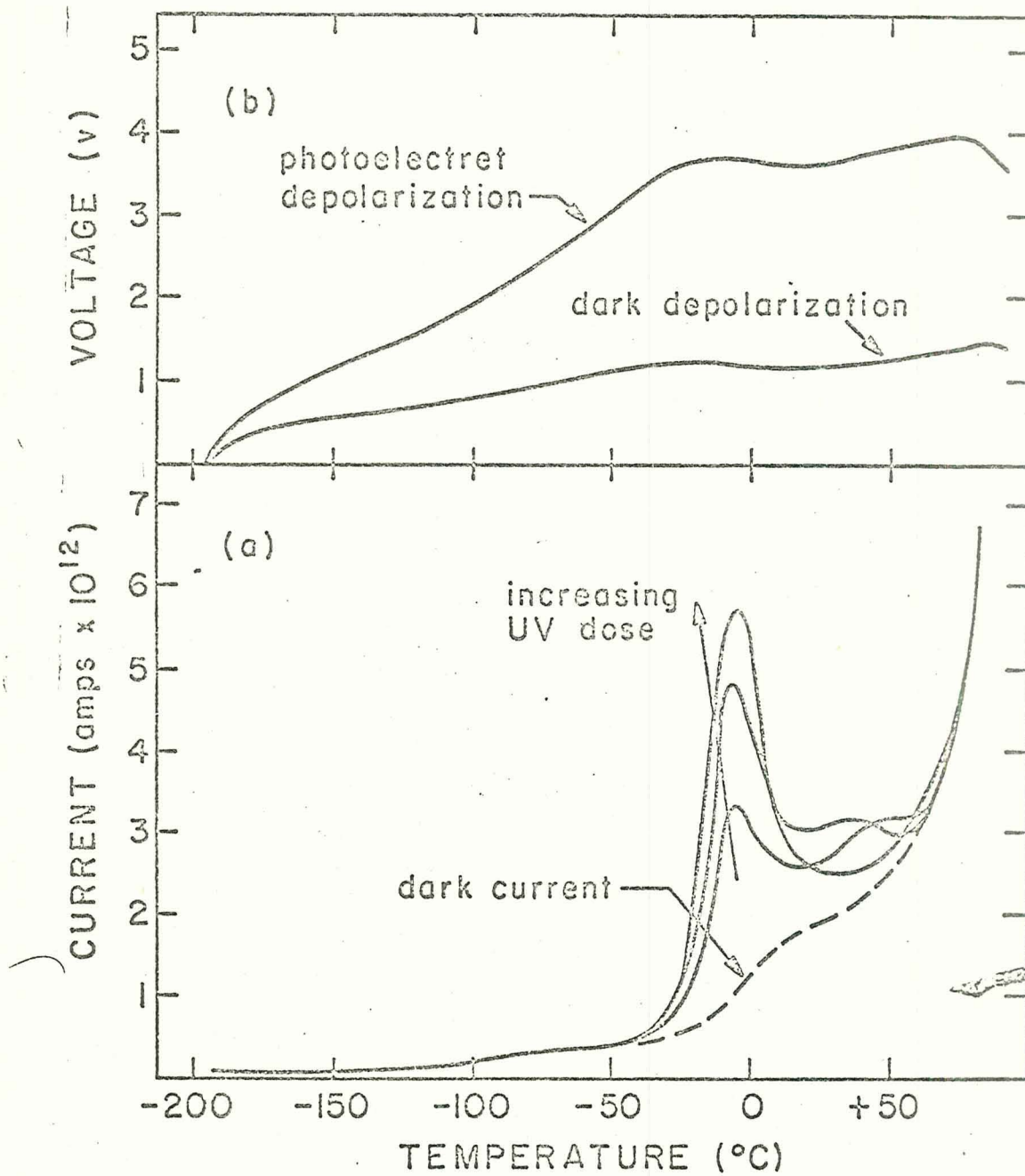
<u>Sample</u>	<u>ΔAlK_{β}</u>	<u>ΔSiK_{β}</u>	<u>ΔOK_{α}</u>
<u>10084.110</u>			
2.8	18	43	190
2.9	48	35	210
3.0	39	23	190
3.1	35	36	290
<u>10085.49</u>	15	65	320
<u>APOLLO 12</u>			
<u>GLASS</u>	22	39	160
<u>High Ti, Fe, Al</u>			
<u>Synthetic</u>			
n = 1.727	30	15	190
n = 1.789	14	50	265

LEGENDS FOR FIGURES

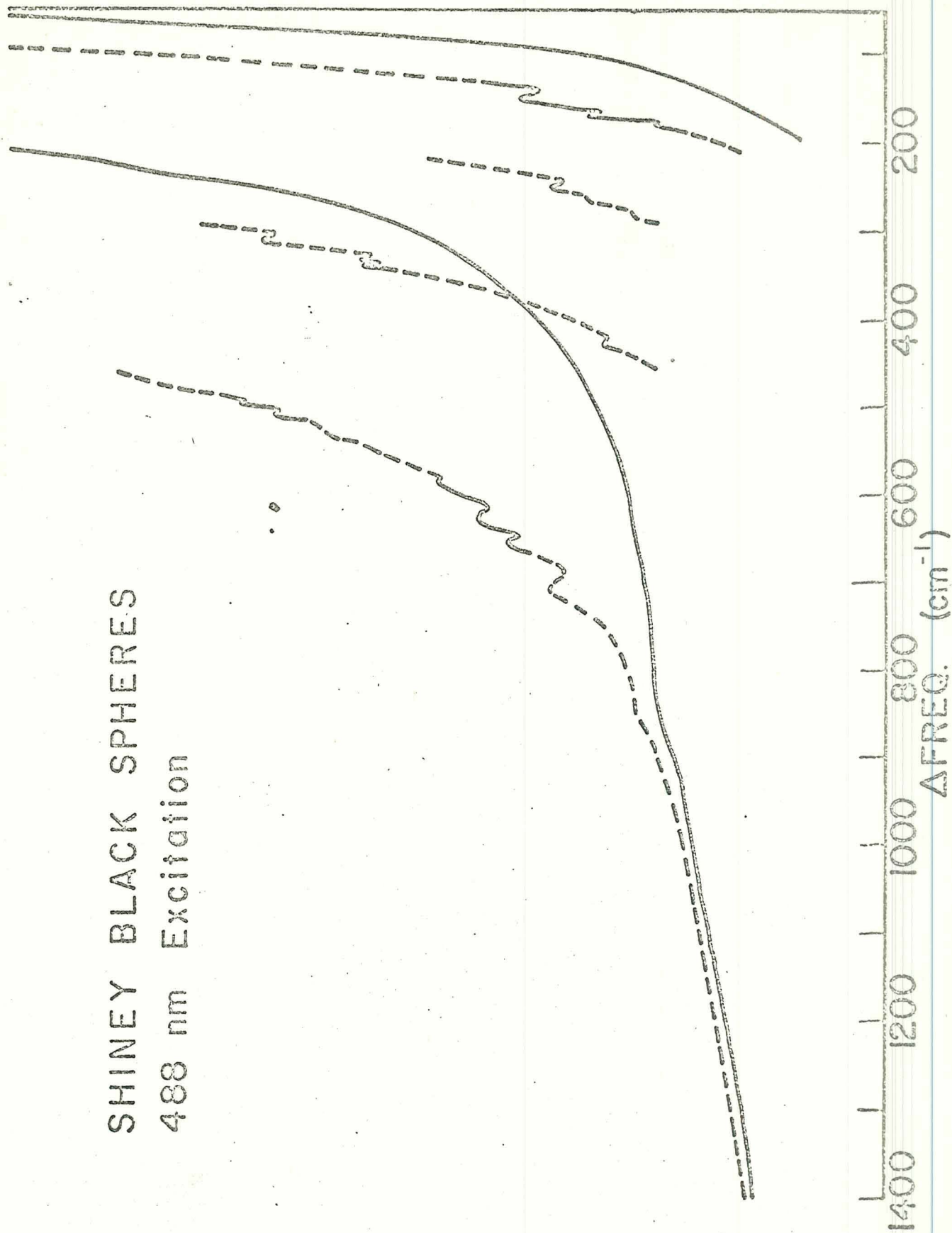
1. Diffuse reflectance spectra of bulk samples of lunar fines. All spectra are adjusted to a base line of the BaSO_4 reference.
2. Transmission spectra of polished slabs of synthetic anorthite glass. Concentrations of transition oxides in weight percent are given on the curves.
3. Electrical measurements on sample No. 12057, 63.
 - (a) thermally stimulated current after different UV exposures.
 - (b) photoelectret depolarization.Heating rate: $30^\circ\text{C}/\text{min}$.
4. Raman spectra of two specimens of black glassy spheres from sample 10084.110. Vertical axis is scattered intensity. Solid curve is a completely glassy specimen; dashed curve indicates recrystallization.
5. Raman spectra of four typical lunar glasses. Both upper curves are for two different fragments (0.1 to 0.3 mm across) of vesicular green-black glass from 10084.110. Apollo 11 and Apollo 12 green glass spectra are each from single particles, 0.1 to 0.3 mm in size, of transparent pale green equant fragments of glass. All spectra are very weak and instrument was operated near the limit of its sensitivity.







SHINEY BLACK SPHERES
488 nm Excitation

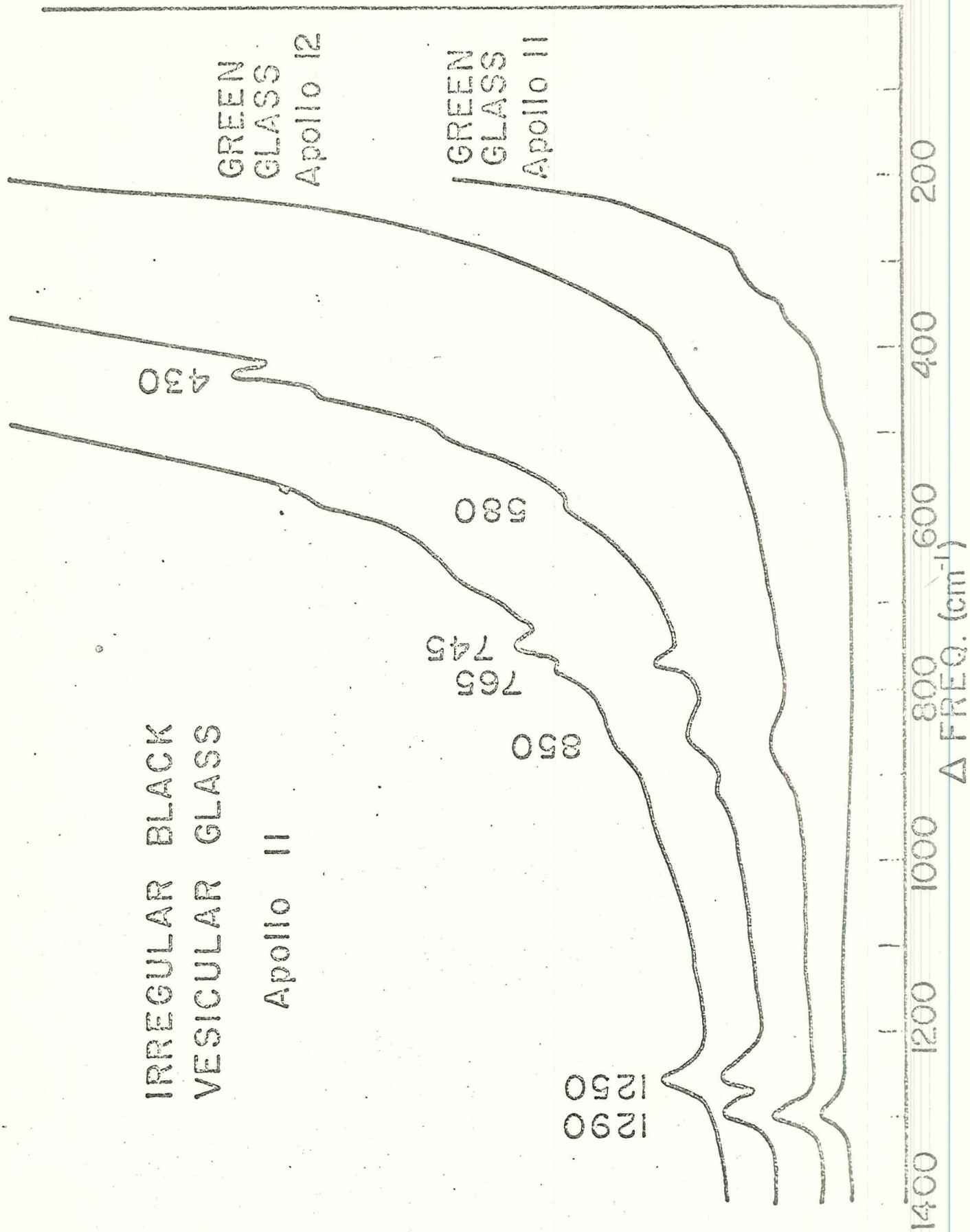


IRREGULAR BLACK
VESICULAR GLASS

Apollo II

GREEN
GLASS
Apollo 12

GREEN
GLASS
Apollo 11



Particle size and shape distributions of lunar fines by CESEMI

by

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ABSTRACT

Size analyses have been carried out on six sets of lunar fines from Apollo 12 by computer evaluation of scanning electron microscope images (CESEMI). The grain size of the particles in the fines range from 400 - 0.2 μm or less. Particle shapes are presented for one sample from ellipses calculated by least square fits to each particle perimeter. Most of the grains are slightly to medium elongated and are quite angular.

INTRODUCTION

Size analyses of Apollo 12 fines have been initiated using recently developed procedures for the computer evaluation of scanning electron microscope images (CESEMI). Details of this approach to morphological characterization of particulate materials have been published recently (MCMILLAN et al. (1969), WHITE et al. (1970a)). This paper briefly outlines the techniques used and presents results on the size distribution analysis for six samples including 12001,1(77), 12003,43, 12033,27, 12042,32, 12057,63, 12070,42 and the shape distribution analysis of sample 12001,1(77).

INSTRUMENTATION

The SEM used in this work is a Japanese Electron Optical, model JSM. The output of the secondary electron detector is an analog signal that generally varies between about -3 to +2 V. This signal is fed, in parallel, to the CRT of the SEM and to the signal preprocessor. The preprocessor module was especially designed in our laboratory to manipulate the secondary electron signal. It consists of a bias level adjust, amplified with gain adjustable continuously from 1 to 10 and a time constant variable continuously from 0 to 10 milliseconds. The output is continuously monitored on a Tektronix scope.

The entire system is shown schematically in Figure 1. The recording instrumentation including the multiplexer, buffer controller, analog to digital converter and tape deck was designed to our specifications by Instrument Technology Corp., Northridge, California. The control module is the ITC Model 8104 B Buffer Controller. The system uses an Astrodats Series 3000 analog to digital converter and a Precision Instrument Corp. Model 1200 digital magnetic tape transport. Various signals from the SEM are fed, in parallel, into a six channel multiplexer, which facilitates the recording of from one to six channels of information simultaneously. The

first channel is generally reserved for the secondary electron signal while the other channels are used for electron backscatter, absorbed electron current and x-ray signals. A six decade thumb wheel switch is used to enter a header of information at the start of each record. When the first raster line of a picture is initiated the system converts analog information from the SEM (secondary electron, electron backscatter, x-ray signals, etc.) into digital data which are recorded in Binary Coded Decimal (BCD) format on seven level magnetic tape. A record gap is automatically inserted at the end of each raster line. This process continues until the end of the last raster line is reached whereupon a end of file is recorded and the recording stops. The tape transport records data at 556 bits per inch at a speed of $37\frac{1}{2}$ inches per second. A single picture composed of 250 lines and 250 sample points per line is recorded in 15 seconds. The input sensitivity is ± 10 V so that the corresponding "gray" scale ranges from -999 to +999. The output is compatible with the University's IBM 360/67 computer.

SPECIMEN HANDLING AND RECORDING

Specimen Preparation

The powders were prepared for SEM image recording in the form of dispersions on aluminum-coated glass slides. The vacuum evaporated aluminum provides a conductive substrate having a perfectly flat surface on the scale of SEM resolution. No conductive overcoat was applied to the specimen. Furthermore, the secondary electron emission intensities from the aluminum are always less than from anywhere on the particles. Thus the particles are always seen as brighter than the background. The powders were dispersed in n-Hexane and transferred to the coated slides. The low surface tension of n-Hexane in contact with air proved to be very advantageous, the evaporation is fast and no residue is left (WEAST (1968)).

Recording Parameters

Secondary electron images were recorded using a SEM voltage of 25 keV and 5×10^{-10} amp specimen current. A picture point density of 250 points

per line and 250 lines was used for all images. The secondary signal is adjusted with the signal preprocessor to give a baseline of about -6 V and a peak on the particles of about +8 V.

Magnification selection is of obvious importance. One does not want to waste tape by recording too many points per particle. Conversely, too low a magnification does not adequately define the smaller particles in a given sample while too high a magnification setting tends to preclude measurement of the largest particles. Six images were recorded for each of the six specimens. Three were at 100X while three were taken at 1000X magnification.

The binary coded map technique used in this study has been described elsewhere (WHITE et al. (1970a), WHITE et al. (1970b)). It involves choosing a signal intensity level and placing an '*' in an array for each data point whose intensity is above the selected level. This array can then be printed and, assuming a correct level was chosen, the binary map will be a replica of what was seen on the oscilloscope at the time of recording. The information collected in this process is then analyzed to produce size and shape characteristics.

RESULTS AND DISCUSSION

Results of the particle size analysis are summarized in Figures 2 and 3. Figure 2 is for the analysis of images taken at 100X magnification. Figure 3 is for results of the analysis at 1000X. On the logarithmic scale is recorded the equivalent circular diameter of the particles, on the probability scale the cumulative frequency of the number of grains.

Under conditions of recording, a particle size truncation occurs at a lower limit of $0.8\mu\text{m}$ in the case of the 1000X images and about $3.0\mu\text{m}$ for the 100X. In view of this truncation, the 1000X results are more complete. Except for the uppermost portions of the curves (about 98% probability), the distributions are very nearly log-normal. The up-turn in the curves above 98% most likely results from the fact that particles which touch or overlap the boundary of the image are not included in the count.

Thus, the largest particles tend not to be included in the curve and this bias has the observed effect on the shape of the distribution. Recordings at 5000X magnification showed the smallest grain size of the particles to be about 0.2 μm . The highest grain size determined with the light microscope of the six samples was around 400 μm .

DUKE et al. (1970) and RABINOWICZ (1970) mentioned that the lunar soil of Apollo 11 is deficient in grains smaller than 15 μm (based on weight fraction and not number count as used in this study). The counting of grains in the analyzed samples (Apollo 12) showed that more than the half of the grains are smaller than 10 μm .

A shape analysis has been made for 55 grains from sample 12001,1(77). The results are given in the Table. The ratio of the major and minor axes (aspect ratio) of the least square fitted ellipse of each particle is a measure of the shape factor (MATSON et al. (1971)). A ratio of one indicates a circular-shaped particle. The larger the ratio the more elongated the particle. From the Table it is seen that the commonly occurring aspect ratio falls in the range 1.60 - 1.89, e.g., the grains are slightly to medium elongated.

With the exception of occasional round glass beads, the particles are typically quite angular. The angularity of the particles and the log-normal size distribution of these samples suggest mechanical comminution without subsequent sedimentary processes to sort and round the material.

ACKNOWLEDGEMENTS

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Table. Aspect ratios of 55 grains (equivalent circular diameter=3.19-6.12 μm) from sample 12001,1(77).

<u>major axis</u> <u>minor axis</u>	% of grains
1.00 - 1.29	16.4
1.30 - 1.59	16.4
1.60 - 1.89	21.8
1.90 - 2.19	5.4
2.20 - 2.49	7.3
2.50 - 2.79	9.1
2.80 - 3.09	7.3
3.10 - 3.39	5.5
3.40 - 3.69	1.8
3.70 - 3.99	1.8
4.00 - 4.29	1.8
4.30 - 4.59	3.6
7.25	1.8

LIST OF FIGURE CAPTIONS

- Figure 1. Block diagram of SEM and digital magnetic tape recording system.
- Figure 2. Size distributions for the six samples generated from the 100X images.
- Figure 3. Size distributions for the six samples generated from the 1000X images.

